



PATENT SPECIFICATION

NO DRAWINGS

1068.783

Date of Application and filing Complete Specification: March 5, 1965.

No. 9467/65.

Application made in France (No. 966,352) on March 6, 1964.

Two Applications made in France (Nos. 980,770 and 980,771) on July 6, 1964.

Complete Specification Published: May 17, 1967.

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Index at acceptance:—C3 P(7C6B, 7C13C, 7D1C, 7D1X)

Int. Cl.:—C 08 f 29/02

COMPLETE SPECIFICATION

Plasticized Crystalline Polyolefin Compositions

5 We, ETHYLENE-PLASTIQUE, a French Body Corporate of 50 rue La Boetie, Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to plasticised crystalline polyolefin compositions, and particularly to plasticised isotactic polybutene, which have different and more advantageous properties than the polyolefins themselves.

15 It is well known that isotactic polyolefins are difficult to plasticise and that isotactic polyolefins plasticised with conventional plasticisers have undesirable properties, particularly in that the plasticiser tends to migrate out of the polyolefin.

20 We have now discovered that isotactic polybutene can be effectively plasticised with certain cyclic hydrocarbons. We have further discovered that isotactic polybutene so plasticised can be used, in turn, to plasticise other isotactic polyolefins. The plasticised polyolefin compositions of the invention have improved fluidity and flexibility and better shock resistance at low temperatures than the corresponding unplasticised polyolefins.

30 According to one aspect of the present invention, therefore, we provide a polymeric composition which comprises isotactic polybutene and, as a plasticiser, at least one C_6 — C_{16} cyclichydrocarbon containing less than 15% of unsaturated bonds and having a boiling point of at least 190°C.

35 According to another aspect of the present invention, we provide a polymeric composition which comprises a mixture of an isotactic polyolefin other than polybutene and a plasticised polybutene composition as described above.

40 The C_6 — C_{16} cyclic hydrocarbons used in accordance with the invention are mono- or polycyclic hydrocarbons which may contain aliphatic side chains; they contain less than

15% of unsaturated bonds in the sense that for every 100 bonds between carbon atoms in such compounds, less than 15 are double bonds. These cyclic hydrocarbons have good resistance to oxidation due to their low unsaturation content and, because their hydrocarbon chains are practically non-polar, they are compatible with polyolefins.

55 Although the C_6 — C_{16} cyclic hydrocarbon used may be a single compound, it is normally preferred to use mixtures of such compounds such as are obtained by vigorously hydrogenating coal tar or a coal tar or petroleum fraction. The hydrogenation product is advantageously freed of most of the oxygenated, hydroxylated, sulphur-containing and nitrogenous impurities it contains before use.

60 It is preferred to use cyclic hydrocarbons of the type described containing from 12 to 16 carbon atoms since these generally have boiling points above 300°C.

65 In the case of isotactic polybutene compositions, the amount of cyclic hydrocarbon plasticiser used is generally from 1 to 50%, based on the weight of the total mixture, and it is preferred that the proportion of plasticiser should be at least 20% on the same basis.

70 As previously described, the plasticised polybutene compositions can be used to plasticise other isotactic polyolefins. These plasticised polyolefin compositions can be obtained either by adding the plasticised polybutene to the isotactic polyolefin or by simultaneously mixing the isotactic polyolefin, isotactic polybutene and the plasticiser. The plasticiser content of the resulting mixture is suitably from 5 to 50% by weight of the total mixture.

75 The plasticised compositions of this invention can be prepared by any suitable method. By way of example, the compositions can be formed by mixing the ingredients in an open mixer at a temperature of from 160° to 180°C for at least 5 minutes.

80 Inorganic or organic additives can be incorporated in the plasticised compositions and,

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- in these cases, the plasticiser content can be increased to as much as 1:1 with respect to the polymer. Such additives, which as is known are particularly well tolerated by polybutene, are used either to reduce the cost price of the compositions or to impart special properties to them, such, for example, as fire retardancy.
- In order that the invention may be more fully understood, the following examples are given by way of illustration only; Examples 3 to 9 illustrate compositions according to the invention and Examples 1 and 2 are given for the purpose of comparison.
- EXAMPLE 1**
- 15 An isotactic polybutene containing anti-oxidant and having the following characteristics:—
- 20 molecular weight 372,000
 % insoluble in ether 97
 melt index (230°C—2.16 kg.) 2.1
 tensile strength 300 kg/cm²
 elongation at break 300%
 torsion rigidity modulus
 at 25°C. 750 kg/cm²
- 25 was mixed for 5 minutes at a temperature of 160—180°C with 20% of di-2-ethylhexyl phthalate. The mixture was then compressed at the same temperature under a light pressure. Forty-eight hours afterwards migration of the plasticiser commenced.
- 30 The properties of the mixture after ageing for 170 hours were as follows:—
- 35 tensile strength 220 kg/cm²
 elongation at break 220%
 torsion rigidity modulus at
 25°C 340 kg/cm².
- EXAMPLE 2**
- 40 The same polybutene as in the previous Example was mixed with 10% of tricresyl phosphate. Mixing was continued for 10 minutes because the polymer absorbed such a quantity of this plasticiser with difficulty. There was no appearance of exudation. The properties after 170 hours were as follows:—
- tensile strength 200 kg/cm²
 elongation at break 200%
 torsion rigidity modulus at
 25°C 490 kg/cm².
- EXAMPLE 3**
- The same polybutene as in Example 1 was mixed under the previously described conditions with 20% of a mixture of cyclic C₉—C₁₄ hydrocarbons having the following characteristics:—
- 50 density at 20°C 0.903 55
 content of unsaturated
 bonds less than 3%
 distillation temperature from 190 to
 280°C.
- The mixture did not exude and after 170 hours had the following properties:—
- 60 tensile strength 290 kg/cm²
 elongation at break 320%
 torsion rigidity modulus at
 25°C 540 kg/cm². 65
- EXAMPLE 4**
- The same materials as in Example 3 were mixed at a plasticiser content of 40%. The properties of the mixture after 170 hours were as follows:—
- 70 tensile strength 220 kg/cm²
 elongation at break 270%
 torsion rigidity modulus at
 25°C 334 kg/cm².
- EXAMPLE 5**
- 75 The same polybutene as in the previous Examples was mixed under the same conditions with respectively 10%, 20%, 30% and 40% of a heavy C₁₂—C₁₆ cyclic hydrocarbon mixture having the following characteristics:—
- 80 density at 20°C 0.970
 content of unsaturated
 bonds less than 12%
 distillation temperature from 300—
 390°C. 85
- The properties of these mixtures after ageing for 170 hours are given in the following table:—

Heavy cyclic hydrocarbon content, %	Tensile strength kg/cm ²	Elongation at break, %	Torsion rigidity modulus at 25° C. kg/cm ²
10	250	300	370
20	210	300	290
30	170	270	220
40	130	240	160

There was no exudation from any of these mixtures.

EXAMPLE 6

5 An isotactic polypropylene having the following characteristics:—

density	0.908
melt index (230°C—5 kg)	20
tensile strength (kg/cm ²)	360
elongation at break	730%
10 modulus of elasticity (kg/cm ²)	12,000

15 was mixed for 5 minutes at 190°C with 20% of a poly-1-butene plasticised with 40% of the heavy hydrogenated C₉—C₁₆ cyclic hydrocarbons of Example 5.

The characteristics of the product obtained were:—

tensile strength (kg/cm ²)	220
elongation at break	200%
20 modulus of elasticity (kg/cm ²)	7,000

EXAMPLE 7

25 The same constituents as in Example 6 were mixed under the same conditions but using 50% of the plasticised poly-1-butene with respect to the total mixture containing isotactic polypropylene.

The mechanical characteristics of the product obtained were:—

tensile strength	280 kg/cm ²
30 elongation at break	440%
modulus of elasticity	3,100 kg/cm ²

EXAMPLE 8

35 A mixture of equal parts of poly-1-butene and isotactic polypropylene was mixed for 5 minutes at 190°C with 40% by weight, with respect to the total mixture, of the heavy hydrogenated cyclic C₉—C₁₆ hydrocarbons of Example 5. The mechanical characteristics of the product obtained were as follows:—

40 tensile strength	180 kg/cm ²
elongation at break	380%
modulus of elasticity	1,580 kg/cm ²

EXAMPLE 9

45 A high density polyethylene having the following characteristics:—

density	0.950
melt index (190°C—2.16 kg)	7
tensile strength	180 kg/cm ²
50 elongation at break	780%
modulus of elasticity	8,200 kg/cm ²

was mixed for 5 minutes at 170°C with 20% of poly-1-butene plasticised with 40% of the heavy hydrogenated C₉—C₁₆ cyclic hydrocarbons of Example 5.

The characteristics of the product obtained were:—

tensile strength	120 kg/cm ²
elongation at break	320%
60 modulus of elasticity	4,100 kg/cm ²

The flexibility of the compositions according to the invention is much better than that of known plasticised mixtures. The permanence of the mechanical properties of polyolefins plasticised in accordance with the invention enables these mixtures to be used for coating various supports, such as papers and textile materials, for the production of films and articles moulded by extrusion, injection, transfer or forming, and for the plasticising of various polyolefins.

WHAT WE CLAIM IS:—

1. A polymeric composition which comprises isotactic polybutene and, as a plasticiser, at least one C₉—C₁₆ cyclic hydrocarbon containing less than 15% of unsaturated bonds and having a boiling point of at least 190°C. 75
2. A polymeric composition according to claim 1, in which the C₉—C₁₆ cyclic hydrocarbon is derived from coal tar or a coal tar fraction or a petroleum fraction. 80
3. A polymeric composition according to claim 1 or 2, in which the plasticiser constitutes from 1 to 50% by weight of the total mixture. 85
4. A polymeric composition according to any of claims 1 to 3, in which the plasticiser constitutes at least 20% by weight of the total mixture. 90
5. A polymeric composition according to any of claims 1 to 4, in which the plasticiser is a C₁₂—C₁₆ cyclic hydrocarbon.
6. A polymeric composition substantially as herein described in any of Examples 3 to 5. 95
7. A polymeric composition which comprises a mixture of an isotactic polyolefin other than polybutene and a composition as claimed in any of claims 1 to 6.
8. A polymeric composition according to claim 7, in which the plasticiser constitutes from 5 to 50% by weight of the total mixture. 100
9. A polymeric composition according to claim 7 or 8, in which the isotactic polyolefin is a high density polyethylene or isotactic polypropylene. 105
10. A polymeric composition, substantially as herein described in any of Examples 6 to 9.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.
—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.